

ROLE OF SOLVENT IN THE INTERACTION OF TCNE/TCNQ WITH COAL

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INTRODUCTION

After N-methyl-2-pyrrolidinone(NMP)-CS₂(1:1, v/v) mixed solvent was found having the magic ability to dissolve coal up to about 60wt% based on daf coal¹, the seeking for higher solubility of coal has never stopped. Enhancement of the coal solubility by adding additives is our way. Up till now, more than 10 additives including electron acceptors and donors were examined²⁻⁵. Electron acceptors, Tetracyanoethylene(TCNE) and 7,7,8,8-Tetracyanoquinodimethane(TCNQ) were found to be two powerful additives. However, the mechanism is still not clear. Previous studies on the mechanism have been concentrated on the charge-transfer complex formation between additives and coal leaving the role of the solvents out of focus^{2,9-10}. However, the attempt to correlate the solubility of coal and the electron acceptor-ability was not successful. Therefore, other mechanism must be involved. In this work, solvent was found strongly related to the mechanism of TCNE/TCNQ to increase the coal solubility.

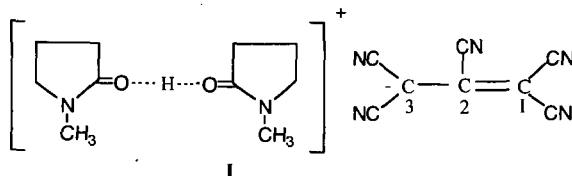
The conclusion of charge-transfer complex formation between coal and TCNE/TCNQ was drawn from the IR shift of ν_{CN} in TCNE/TCNQ when they were mixed with coal in solvent. We have reported that the coal containing TCNE deposited from NMP-CS₂(1:1, v/v) mixed solvents had a pair of IR band at 2200cm⁻¹ and 1500cm⁻¹¹². Initially, the band at 2200cm⁻¹ had been proposed arising from charge-transfer complex between TCNE and coal⁶. However, further investigation found that the two IR bands arisen from the reaction product of TCNE and NMP, i.e., NMP 1,1,2,3,3-pentacyanopropene salt(NPCNP). TCNE does not exist as a neutral molecule in NMP, instead, an anion derivative of TCNE was formed, which may be the key component to enhance the coal solubility. Addition of NPCNP was found also effective for the coal solubility increase.

In the case of TCNQ, the interaction of TCNQ with coal aromatics seems to be related to the solvent used. TCNQ radical anion generated in NMP may be an intermediate of TCNQ interaction with coal aromatics. The extent of TCNQ interaction with coal aromatics depends on the structure of aromatics.

EXPERIMENTAL

UV spectral properties of TCNE/TCNQ in various solvents were measured on HITACHI U2000 UV spectrometer with 1 cm quartz cell. FTIR spectra were recorded on JASCO FT/IR-8300 spectrometer using KRS-5 or KCl cell(thickness of 0.1mm), 16 scans at resolution of 4cm⁻¹. NMR measurement was carried out on JEOL JNM-LA400 spectrometer. CDCl₃ was used as solvent. All the solvents used for spectral analysis are spectrophotometric grade. "Anhydrous" NMP was dehydrated by 4 Å molecular sieves overnight.

The procedure of the reaction of TCNE with NMP in the presence of water referred to that of TCNE reaction with pyridine in the presence of water⁸, but it was carried out at room temperature. 30mL acetone containing 6.3g TCNE was added into 100ml NMP containing 10% water under N₂ protection. After the reaction, acetone and NMP were removed via a rotary evaporator at 40°C and large volume of diethyl ether was decanted into reactor. A yellow solid was obtained(yield, 58wt%, based on raw product). Recrystallization of a portion of the solid from diethyl ether gave a yellow crystal of **I**, mp 51-52°C: UV-visible(NMP) λ_{max} nm(log ϵ) 400(4.41), 418(4.40); FTIR(thin film, cm⁻¹) 1519(ν_{C-C}), 2203($\nu_{C\equiv N}$); (liquid film) 2199(in NMP, $\nu_{C\equiv N}$); ¹H-NMR(CDCl₃) δ 3.70, 3.06, 2.77, 2.24ppm, a broad and weak peak at 7.5-11ppm downfield shift as the increase of concentration of **I**; ¹³C-NMR(CDCl₃) δ 178.32, 135.60, 116.70, 114.06, 113.78, 57.91, 51.95, 31.26, 30.46, 17.38ppm. Anal. Calcd for NMP-1,1,2,3,3-Pentacyanopropene salt(**I**, C₁₈H₂₀N₇O₂): C, 59.02%; H, 5.29%; N, 26.75%; O, 8.78%. Found: C, 59.18%; H, 5.46%; N, 26.78%; O, 8.74%.



RESULTS AND DISCUSSION

Spectra properties of TCNE-NMP system

The shift of stretching frequency of $C\equiv N(\nu_{CN})$ of TCNE in some solvents indicates that TCNE may react or interact with solvents (Table 1). In acetone and THF, almost no shift was observed. The small shift in toluene is attributed to the formation of charge-transfer complex of TCNE with toluene. However, the large shift of ν_{CN} in NMP indicates that TCNE does not exist as a neutral molecule in this solvent. Instead, a new substance may be generated by the reaction of TCNE with NMP. In dehydrated NMP, ν_{CN} shifts to 2338cm^{-1} arose from complex of TCNE-NMP, while in commercial NMP (used for extraction) containing very small amount of water (estimated from the hydroxyl band), the ν_{CN} band appears at 2199cm^{-1} , which indicates the presence of PCNP anion.

Figure 1 shows the change of UV spectra of TCNE in NMP of different water content. In dehydrated NMP, PCNP anion absorptions at 400 and 418nm are very weak. However, they are increasing but the peak of TCNE-NMP complex at 298nm decreasing as the increase of water content in NMP, indicating that PCNP anion is generated from the reaction of TCNE with NMP in the presence of water.

The reaction of TCNE with pyridine⁸ or pyridone¹¹⁻¹² to generate PCNP anion was known 30 years ago, but the reaction of TCNE with NMP to generate the same anion is found first time.

Although this reaction needs water, commercial grade NMP used for extraction usually contains small amount of water. Based on our experimental procedure, 1 gram coal or PI was added 0.2mmol TCNE in 60 mL NMP-CS, mixed solvent (1:1, v/v), 0.012wt% water in NMP is enough for 0.2mmol TCNE to generate PCNP anion. Although we have not measured the water content of the NMP, it is quite possible that 97% commercial grade NMP used for extraction contains enough water for the reaction. Moreover, NMP is very easy to absorb water. It is very difficult to remove all the water from NMP. Even dehydrated NMP was used, PCNP anion band at 400 and 418nm is still observable (Figure 1) in TCNE-NMP system. This is probably due to incomplete dehydration by molecular sieves or re-absorption of water during the operation. It was also found that in commercial NMP, ν_{CN} of TCNE in NMP always shifts to 2199cm^{-1} . These results demonstrate that TCNE exists as PCNP anion in NMP but not neutral TCNE molecule.

Effect of 1,1,2,3,3-pentacyanopropene(PCNP) anion to increase the solubility of PI

Based on the spectral study, TCNE does not exist as a neutral molecule in NMP as well as in the NMP-CS, mixed solvent. Instead, NPCNP is formed. The solubility of PI and its parent coal(UF) in the NMP-CS, mixed solvent was examined by adding small amount of NPCNP. Figure 2 shows that the addition of only 0.04mmol/g-PI NPCNP is enough to increase the solubility of PI from 54% to 96%; more NPCNP, 0.2mmole/g-PI, results in 99.9% solubilization of PI. The addition of 0.2mmol/g-coal NPCNP increases the UF coal solubility from 64.6% to 71.5%, which is closed to the increment by adding the same amount of TCNE³. Another PCNP anion contained compound, Pyridinium 1,1,2,3,3-pentacyanopropenide, which was synthesized from pyridine and TCNE in the presence of water⁸, was also found effective to enhance the solubility of PI. The two experiments indicate that PCNP anion is the key component to enhance the solubility of coal.

The mechanism of PCNP anion to enhance coal solubility is believed to be attributed to breaking hydrogen bonding. NMR study confirms the possibility of this anion being able to break the hydrogen bonding formed between pyridine and phenol. The details will be reported in a paper submitted to Energy Fuels.

Spectral property of TCNQ in various solvents

The UV-visible spectra property of TCNQ depends on solvent, as shown in Figure 3. It is quite different in NMP and pyridine than in THF and chloroform. The peaks around 800nm, i.e., 752, 771 and 833, 854nm, were assigned to the TCNQ radical anion¹³⁻¹⁴. Figure 3 illustrates that TCNQ generates TCNQ radical anion in NMP and pyridine but not in THF and chloroform.

In the room temperature, the addition of aromatics into the NMP solution containing TCNQ results in the change of its UV-visible spectrum. As shown in the Figure 4, the absorption of TCNQ radical anion around 800nm disappeared as accompanied by appearing a new absorption at 490nm, which may be arisen from the complex formed between TCNQ and aromatics. However, when the aromatics were added into the mixture of TCNQ and chloroform, chlorobenzene or THF, no such change occurs. The spectra are just a summation of the TCNQ-solvent and aromatics. Accordingly, we can not deny the possibility that TCNQ reacts with aromatics by the TCNQ radical anion as an intermediate.

The extent of TCNQ reaction with the aromatics depends on the structure of aromatics. Phenanthrene reacts with TCNQ radical anion quickly, the peaks around 800nm disappeared in several minutes after it was added into the mixture of TCNQ-NMP and a new peak at 490nm appeared. However, anthracene, the isomer of phenanthrene, is hard to react with TCNQ radical at room temperature. The spectrum has no change even after 180min. The larger size

aromatics, pyrene, can react with the TCNQ radical anion, but it takes longer time than phenanthrene needed. The different distribution of π electrons on the aromatic ring may cause the difference. Coal from different source and rank contains aromatics of different ring size and structure, which may cause the selective effect of TCNQ for certain coal, e.g., TCNQ is effective for some coals but not effective for others.

When pyridine insoluble fraction(PI) from Upper Freeport coal extracts(extraction with CS_2 -NMP mixed solvent, 1:1 by volume) was used instead of pure aromatics to repeat the experiment mentioned above, similar spectra changes were observed. As the reaction time increase, the absorption of TCNQ radical anion around 800nm decreased but the absorption at 490nm increased(see Figure 5). Based on the results of pure aromatics, aromatics in PI reacts with TCNQ radical anion to generate a new complex(around 490nm) is concluded.

CONCLUSIONS

The importance of solvent was noted in examination the mechanism of TCNE/TCNQ to enhance the coal solubility. TCNE was found not to be existed as a neutral molecule in NMP. Instead, it reacts with NMP in the presence moisture to generate 1,1,2,3,3-pentacyanopropene (PCNP) anion, which is considered a key component to enhance the coal solubility by breaking coal-coal interaction, e.g., hydrogen bonding. TCNQ generates TCNQ radical anion in NMP and pyridine, which is an intermediate of TCNQ interaction with coal aromatics.

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Table I. List of TCNE in various solvent

solvent	$\nu_{\text{CN}}(\text{cm}^{-1})$
blank	2260
acetone	2257
THF	2257
toluene	2252
NMP ^a	2338
NMP ^b	2199

^adehydrated by 4 Å molecular sieves;

^bcommercial one(NMP content 97%) containing small amount water(estimated from the weak hydroxyl band in the spectrum).

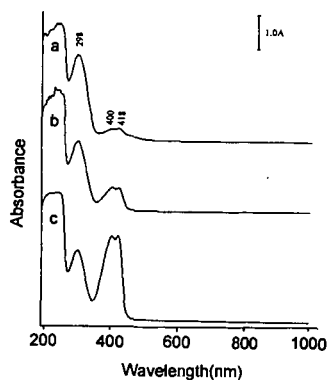


Fig. 1. UV-visible spectra of TCNE in NMP containing water(mg/mL). a, 0; b, 15; c, 50

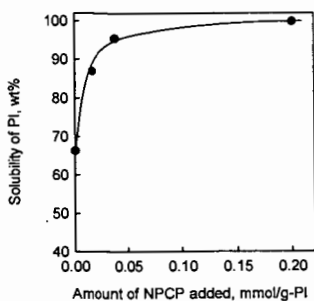


Fig. 2. Increase of the solubility of PI(pyridine insoluble fraction) from Upper Freeport coal in the NMP-CS₂ mixed solvent by adding NPCNP

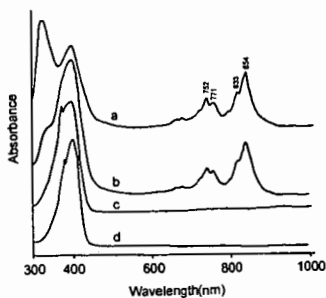


Fig. 3. UV-visible spectra of TCNQ in various solvents.

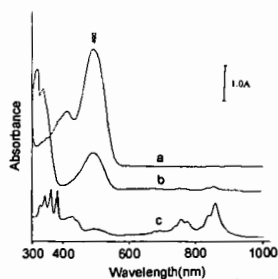


Fig. 4. UV-visible spectra of aromatics($1 \times 10^{-5} \text{ mole L}^{-1}$) in $5 \times 10^{-3} \text{ mole L}^{-1}$ TCNQ NMP solution.
a, phenanthrene(reaction for 3 min); b, pyrene(40 min); c, anthracene(180 min)

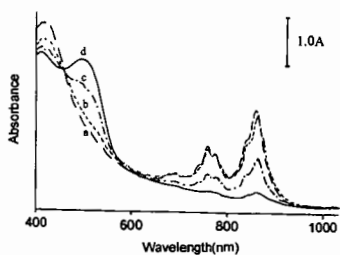


Fig. 5. UV-visible spectra of PI-TCNQ-NMP-CS₂(1:1, v/v) system.
a, 0 min; b, 30 min; c, 60 min; d, 90 min